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(54) Title of the Invention:

PROCESS FOR THE PRODUCTION OF EPOXIDES FROM OLEFINS,
HYDROGEN, AND OXYGEN

(57) Abstract:

Production of epoxides from olefins, hydrogen, and oxygen with the use of an oxidation catalyst based on titanium or vanadium silicalites with a zeolite structure and a content of 0.1-20 wt.% of platinum metals, in which the platinum metals are present in each case in at least two different bond energy states, possibly in the presence of an inert carrier gas from the group consisting of nitrogen,

noble gases, carbon dioxide, and C_1 - C_8 -hydrocarbons, where the molar ratio of hydrogen to oxygen is 1:1-1:10, the molar ratio of inert carrier gas to olefin can be as much as 20:1, and the molar ratio of oxygen to olefin or to the sum of olefin and any C_1 - C_8 -hydrocarbon which may be present as an inert carrier gas is less than 1:3-1:20.

The following information has been taken from documents submitted by the applicant.

S P E C I F I C A T I O N

The present invention pertains to an improved process for the production of epoxides from olefins, hydrogen, and oxygen by means of an oxidation catalyst based on titanium or vanadium silicalites with a zeolite structure and with a content of platinum metals, possibly in the presence of an inert carrier gas and under maintenance of certain concentration ranges for the educts and the inert carrier gas.

Platinum metal-containing titanium silicalites are known as oxidation catalysts. For example, the hydroxylation of benzene and hexane on palladium-containing titanium silicalites is described in *J. Chem. Soc. Chem. Commun.*, pp. 1,446-1,447, 1992 (1). JP Kokai No. 4[1992]-352,771 (2) pertains to the production of propylene oxide from propylene, hydrogen, and oxygen with the use of a palladium-containing titanium silicalite catalyst.

From German Patent Application No. P. 4,425,672.8 (3), published subsequently, another process for the production of epoxides from olefins, hydrogen, and oxygen by means of the cited oxidation catalyst based on titanium or vanadium silicalites with a zeolite structure with a content of platinum metals is known. This process can be carried out in the presence of a carrier gas such as nitrogen. The molar ratio of oxygen to olefin is 1:1-1:3 in this case.

Epoxidation processes of this type with the described oxidation catalysts known in accordance with the state of the art, however, suffer from certain disadvantages. In many cases, the catalysts are suitable only for a narrowly circumscribed purpose. The selectivity, conversion, space-time yield, and service lives are also often parameters which require improvement. In addition, safety aspects such as operation outside the explosion range of the educts and gases used are criteria which are crucial with respect to the industrial use of such catalysts.

The task of the present invention was to provide a process for the epoxidation of olefins which no longer suffers from the disadvantages of the state of the art and which in particular makes possible longer catalyst service lives and safe operation.

Accordingly, a process for the production of epoxides from olefins, hydrogen, and oxygen with the use of an oxidation catalyst based on titanium or vanadium silicalites with a zeolite structure and a content of 0.01-20 wt. % of one or more platinum metals selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, and platinum, in which the platinum metals are in each case present in at least two different bond energy states, and possibly in the presence of an inert carrier gas selected from the group consisting of nitrogen, noble gases, carbon dioxide, and C_1 - C_8 -hydrocarbons, where the molar ratio of hydrogen to oxygen is 1:1-1:10 and the molar ratio of inert carrier gas to olefin can be as much as 20:1, has been discovered, which is characterized in that the molar ratio of oxygen to olefin or to the sum of olefin and any C_1 - C_8 -hydrocarbon which may be present as inert carrier gas is less than 1:3-1:20. [*Hard to distinguish between C_8 and C_8 -- Tr. Ed.*].

The gases which are suitable as inert carrier gases include not only

nitrogen and carbon dioxide but also noble gases such as helium, neon, argon, krypton, and xenon as well as saturated and unsaturated hydrocarbons with 1-8, especially with 1-6, and preferably with 1-4 C atoms such as methane, ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane, neopentane, *n*-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, *n*-heptane, *n*-octane, cyclohexane, cyclopentane, benzene, toluene, xylenes, and ethylbenzene. Nitrogen and saturated C₁-C₆-hydrocarbons are the preferred inert carrier gases, and mixtures of the listed inert carrier gases can also be used.

In accordance with the present invention, therefore, a procedure is made possible which is outside the explosive limits, because the olefin to be reacted — possibly in a carrier gas stream or circulating gas stream of, for example, a suitable hydrocarbon — is supplied in such a way that the olefin or the sum of olefin and a carrier gas such as a hydrocarbon is present in sufficient excess versus oxygen and hydrogen that no explosive mixture can form either in the reactor or in the feed and discharge lines.

Specifically in the epoxidation of propylene to propylene oxide according to the invention, propane can be supplied so that the upper explosion limits of mixtures of propylene, propane, hydrogen, and oxygen are safely exceeded.

Before the oxidation catalyst is used, it contains the platinum metals in the cited special modification of a mixture of various bond energy states. The various bond energy states correspond formally to different oxidation stages of the metals. In a preferred embodiment, two, three, four, or five different bond energy states are present.

In the presence of two different bond energy states, the mixture can con-

sist, for example, of species of oxidation stages 0 and +1, of 0 and +2, of 0 and +3, or of 0 and +4. The two species are usually in a ratio of 5:95-95:5, and especially of 10:90 to 90:10.

In the presence of three different bond energy states, the mixture can consist, for example, of species of oxidation stages 0, +1, and +2; of 0, +2, and +3; of 0, +2, and +4; of 0, +1, and +3; of 0, +1, and +4; or of 0, +3, and +4. The three species are usually in a ratio of (0.05-20):(0.05:20):1, and preferably (0.1-10):(0.1-10):1.

In addition, mixtures of four or more different oxidation stages can be present, such as mixtures of 0, +1, +2, and +3; of 0, +1, +2, and +4; of 0, +2, +3, and +4; of 0, +1, +3, and +4; or of 0, +1, +2, +3, and +4. The species are in this case present in similar weight ratios to each other as in the mixtures of 2 or 3 different oxidation stages.

Among the platinum metals, palladium is preferred. In an especially preferred embodiment, the palladium is present in two or three different bond energy states.

The easiest way to characterize the bond energy states on the surface of the catalyst is by x-ray photoelectron microscopy (XPS). For example, in a typical mixture of three palladium species, the corresponding values for the energies of the Pd 3d-state are at 335.0-335.4 eV, 336-336.6 eV, and 337.1-337.9 eV, which corresponds formally to the oxidation stages Pd⁰, Pd¹⁺, and Pd²⁺.

For the oxidation catalysts according to the invention, it is especially advantageous to apply the platinum metals in such a way that no metal-metal bonds become active and so that metal-zeolite bonds are the dominant type. In particular, it can be seen from studies of the fine x-ray structure (EXAFS)

[*Extended X-Ray Absorption Fine Structure -- Tr. Ed.*] that, when palladium is used, it is essential that palladium-oxygen bond distances of 2.02 ± 0.02 Å be almost the only ones present and that the palladium-palladium distances of 2.74 ± 0.02 Å such as those in extended palladium-metal or palladium agglomerates and palladium-palladium distances of 3.04 ± 0.02 Å such as those present in palladium(II) oxide be avoided.

The basis of the oxidation catalyst used here is formed by titanium or vanadium silicalites with a zeolite structure, preferably with the pentasil zeolite structure, and especially the types which can be assigned radiographically to the MFI, MEL, or MFI/MEL mixed structure. Zeolites of this type are described in, for example, W. M. Meier and D. H. Olson's *Atlas of Zeolite Structure Types*, Butterworths, 2nd ed., 1978. Titanium-containing zeolites with the structure of ZSM-48, ferrierite, ZSM-12, or β -zeolite; mordenite; and meso-porous titanium-containing metal oxides according to EP-A No. 670,286 or US-A No. 5,057,296 are also conceivable.

In the process according to the invention, the titanium of the catalyst can be partially or completely replaced by vanadium. The molar ratio of titanium and/or vanadium to the sum of silicon plus titanium and/or vanadium is usually in the range of 0.01:1-0.1:1.

The content of the cited platinum metals in the above-cited oxidation catalyst is 0.01-20 wt.%, preferably 0.1-10 wt.%, and even more preferably 0.2-5 wt.%, based on the total weight of the oxidation catalyst.

The oxidation catalyst described can be modified not only with the cited platinum metals but also with one or more elements from the group consisting of iron, cobalt, nickel, rhenium, silver, and gold. These elements are then usually present in an amount of 0.01-10 wt.%, and especially 0.05-5 wt.%,

based on the total weight of the oxidation catalyst.

The oxidation catalyst used in the process according to the invention is advisably produced by impregnation or reaction of titanium or vanadium silicalites with a zeolite structure with salt solutions, chelate complexes, or carbonyl complexes of the platinum metals. The production method is characterized in that, following the impregnation or reaction, the required distribution of the bond energy states of the platinum metals is adjusted by the use of suitable reducing or oxidizing conditions.

For example, the platinum metals can be applied by impregnation with a platinum metal salt solution, especially in the oxidation stages of +2 to +4, from a purely aqueous, a purely alcoholic, or an aqueous-alcoholic mixture at temperatures of 20-90°C, especially of 30-55°C. The salts which can be used include, for example, the corresponding chlorides, acetates, or their tetramine complexes. In the case of palladium, suitable salts include palladium(II) chloride, palladium(II) acetate, and the palladium(II) tetraminochloro complex. The quantity of metal salt is to be selected so that concentrations of 0.01-20 wt.% of platinum metal are obtained on the resulting oxidation catalyst.

It is also possible to carry out a reaction in a nonpolar solvent with appropriate chelate complexes of the platinum metals, such as, for example, with acetylacetonates, acetonylacetonates, or phosphine complexes.

It is also possible to apply the platinum metal in the form of the corresponding carbonyl complex of the metal. In this case, it is advisable to work in the gas phase under elevated pressure or to carry out the impregnation with these carbonyl complexes in a supercritical solvent such as CO₂.

After a possible drying process and/or possibly after a calcination of

the catalyst precursor thus obtained, the distribution of the bond energy states is preferably adjusted by partial reduction of any existing higher oxidation stages of the platinum metals, especially by hydrogenation in a hydrogen atmosphere. If the platinum metals are already in oxidation stage 0, as they would be when applied as carbonyl complexes, they must then be partially oxidized.

In a preferred embodiment, the oxidation catalyst according to the invention is impregnated with salt solutions of the platinum metals in oxidation stages +2 to +4, and then the dried catalyst is hydrogenated in a hydrogen atmosphere. This production procedure is characterized in that the hydrogenation is carried out at temperatures of 20-120°C, preferably at 25-100°C, and even more preferably at 30-70°C.

If the temperature is too high during this partial reduction by hydrogenation in a hydrogen atmosphere, the platinum metals will be present almost exclusively in oxidation stage 0, that is, as metals, and in the form of relatively large agglomerates, which can be detected in the micrograph as the presence of metal clusters larger than 1.0 nm in size.

The above-cited titanium or vanadium silicalites with a zeolite structure, especially those with the MFI-pentasil structure, are usually produced by crystallizing a synthesis gel consisting of water, a titanium or vanadium source, and silicon dioxide in some suitable manner with the addition of organic nitrogen-containing compounds ("template compounds") under hydrothermal conditions and possibly under the addition of ammonia, alkali, or fluoride as mineralizer. The organic nitrogen-containing compounds which can be used include, for example, 1,6-diaminohexane and the salts or the free hydroxide of tetraalkylammonium, specifically of tetrapropylammonium.

In the production of the titanium or vanadium silicalites, contamination with large amounts of alkali or alkaline-earth metal compounds must be avoided. Alkali contents (especially of sodium or potassium) of < 100 ppm are desirable, so that later a sufficiently active oxidation catalyst can be obtained.

The crystallization of the phase-pure structure of the titanium or vanadium silicalite is preferably carried out at temperatures of 140-190°C, especially at 160-180°C, over a period of 2-7 days, well-crystallized product being obtained in only about 4 days. By means of vigorous agitation and a high pH value of, for example, 12-14 during crystallization, the synthesis time and the crystallite size can both be significantly reduced.

For example, primary crystallites with particle diameters in the range of 0.05-0.5 μm and especially those with an average particle size of less than 0.2 μm are advantageous.

After crystallization, the titanium or vanadium silicalite can be filtered off, washed, and dried at 100-120°C by methods known in themselves.

To remove the amine or tetraalkylammonium compounds still present in the pores, the material can also be subjected to a thermal treatment in air or under nitrogen. It is advantageous in this case to burn off the template under conditions which limit the temperature increase to values of < 550°C.

The modifications to which the oxidation catalyst according to the invention can be subjected include not only the previously mentioned additions of platinum metals and other elements but also the methods already known according to the state of the art for shaping with the help of a binder, for ion-exchange, and for surface modification such as by chemical vapor deposition (CVD) or chemical derivitization such as silylation.

The presence of the catalyst functions required for an oxidation reaction can be checked by IR spectroscopy: in the case of titanium-containing zeolites with the MFI structure, significant bands occur at 550 cm^{-1} and at 960 cm^{-1} , for example, which indicate the presence of the desired solid-state crystallinity and of the required oxidation activity.

Depending on the olefin to be reacted, the epoxidation according to the invention can be carried out in the liquid phase, in the gas phase, or in the supercritical phase. When liquids are used, the catalyst is preferably in the form of a suspension, whereas in the case of gas-phase and supercritical procedures, a fixed-bed arrangement is advantageous.

If epoxidation is carried out in the liquid phase, it is advantageous to work at a pressure of 1-10 bars, with a suspension, and in the presence of solvents. Suitable solvents are alcohols such as methanol, ethanol, isopropanol, and *tert*-butanol, or mixtures thereof, and especially water. It is also possible to use mixtures of the cited alcohols with water. In certain cases, the use of water or of an aqueous solvent system brings about a significant increase in selectivity for the desired epoxide in comparison with the use of pure alcohols as solvent.

Epoxidation according to the invention is usually carried out at temperatures ranging from -5°C to $+70^{\circ}\text{C}$, preferably at temperatures in the range of $20-50^{\circ}\text{C}$. The molar ratio of hydrogen to oxygen can usually be varied in the range of $\text{H}_2:\text{O}_2 = 1:10-1:1$ and is especially favorable at $1:5-1:1$, and even more especially at $1:2.5-1:1$.

As an essential feature of the invention, the molar ratio of oxygen to olefin or to the sum of olefin and any C_1-C_8 -hydrocarbon which may be present, especially a saturated C_1-C_8 -hydrocarbon, as inert carrier gas, is less

than 1:3-1:20, preferably 1:4-1:10, and even more preferably 1:5-1:7. "Less than 1:3" means that the molar amount of olefin or olefin-hydrocarbon mixture present must be more than three times greater than the molar amount of oxygen.

If an inert carrier gas is used concomitantly, the molar ratio of inert carrier gas to olefin is usually in the range of 1:50-20:1, and especially 1:20-1;1.

A significant increase in the service life of the catalyst is associated with the process according to the invention for managing the reaction with an excess of olefin and possibly of hydrocarbon as inert carrier gas relative to hydrogen and oxygen.

The olefin used can be any desired organic compound which contains at least one ethenic unsaturated double bond. It can be aliphatic, aromatic, or cycloaliphatic in nature; it can have a linear or a branched structure. The olefin preferably contains 2-30 C atoms. More than one ethenic unsaturated double bond can be present, such as those found in dienes or trienes, for example. The olefin can also contain functional groups such as halogen atoms, carboxyl groups, carbon ester [carbonates? -- Tr. Ed.] functions, hydroxyl groups, ether linkages, sulfide linkages, carbonyl functions, cyano groups, nitro groups, or amino groups.

Typical examples of olefins of this type are ethylene, propylene, 1-butene, *cis*- and *trans*-2-butene, 1,3-butadiene, pentenes, isoprene, hexenes, octenes, nonenes, decenes, undecenes, dodecenes, cyclopentene, cyclohexene, dicyclopentadiene, methylenecyclopropane, vinylcyclohexane, vinylcyclohexene, allyl chloride, acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid, allyl alcohol, alkyl acrylates, alkyl methacrylates, oleic acid, linoleic acid, linolenic acid, esters and glycerides of these unsaturated fatty

acids, styrene, α -methylstyrene, divinylbenzene, indene, and stilbene. Mixtures of the listed olefins can also be epoxidized by the process according to the invention.

The process according to the invention is suitable in a very particular way for the epoxidation of propylene to propylene oxide. Through the selection of suitable compositions of the educts and possibly of carrier gas and through the use of suitable pressures, the reaction can be conducted outside the explosive limits.

It is also easy to regenerate the oxidation catalyst according to the invention. Deactivated catalysts can be restored to their active form by controlled burning-off of carbon deposits in the temperature range of 350-650°C, followed by reduction with, for example, hydrogen.

If the deposits are thin, the catalyst can also be regenerated simply by washing it. Depending on the requirements, this can be carried out in the neutral, acid, or basic pH range. If desired, the catalyst can also be regenerated by means of a solution of hydrogen peroxide in a mineral acid.

The following examples are intended to describe the invention in greater detail and are not to be understood as limiting it in any way.

Actual Example 1

This example describes the crystallization of a titanium silicalite.

For this purpose, 455 g of tetraethyl orthosilicate was loaded into a four-neck flask (with a capacity of 2 L); 15 g of tetraisopropyl orthotitanate was then added from a dropping funnel over the course of 30 minutes with stirring (250 rpm, paddle stirrer). A clear, colorless mixture formed. Then 800 g of a 20 wt.% aqueous solution of tetrapropylammonium hydroxide (alkali con-

tent < 10 ppm) was added, and the mixture was stirred for another hour. The alcohol mixture which had formed by hydrolysis (about 450 g) was distilled off at 90-100°C. 1.5 L of deionized water was added, and then the sol, which by then had become slightly opaque, was transferred to a 2.5-L stirred autoclave. The sealed autoclave (anchor stirrer, 200 rpm) was brought to a reaction temperature of 175°C at a heating rate of 3°C/min. After 92 hours, the reaction was terminated. The cooled reaction mixture (a white suspension) was centrifuged off and washed several times with water until neutral. The solid material thus obtained was dried at 110°C for 24 hours (final weight, 149 g). Then the template still present in the zeolite was burned off in air at 500°C for 5 hours (loss on calcination, 14 wt.%).

According to wet-chemical analysis, the pure-white product had a Ti content of 1.5 wt.% and a residual alkali content (potassium) of < 0.01 wt.%. The yield (based on the amount of SiO₂ originally used) was 97%. The crystallite size was about 0.1-0.15 μm, and the product showed typical bands at 960 cm⁻¹ and 550 cm⁻¹ in the IR spectrum.

Actual Example 2

For the impregnation with palladium, first a flesh-colored solution was prepared from 0.515 g of palladium(II) chloride and 120 g of ammonia solution (25 wt.% in water) with stirring at room temperature. 60 g of the freshly prepared titanium silicalite from Actual Example 1 was suspended in 130 g of deionized water in a round-bottom flask. The total amount of prepared Pd-tetraminochloro complex solution was added to this, and the mixture was stirred for 1 hour in a rotary evaporator at room temperature under normal pressure. The suspension was then evaporated under vacuum (5-19 mbars) at

60°C. The white product was sent on directly to the reduction step.

In a laboratory rotary tube furnace (quartz glass; diameter, 5 cm; length of heating zone, 20 cm), 20 g of the Pd-impregnated product was reduced over the course of 90 minutes at a temperature of 50°C with a gas mixture of 20 L/h of nitrogen and 1 L/h of hydrogen at a rotational speed of the furnace of 50 rpm.

The finished product was light in color and, on analysis by transmission-electron microscopy (TEM), showed no metallic palladium clusters with a size of more than 1.0 nm. The palladium content was determined by wet-chemical analysis to be 0.49 wt.%. By means of XPS, the three previously cited bond energy states of the Pd-3d_{5/2} photoelectron (corresponding formally to oxidation stages +2, +1, and 0) were found.

Comparison Example 3

This comparison example explains the one-stage production of propylene oxide from propylene, hydrogen, and oxygen on the catalyst produced according to Actual Examples 1 and 2 with methanol as solvent by the "lean" method with less than the required amount of propylene.

0.76 g of the catalyst from Actual Example 2 was suspended with stirring in 1,730 mL of methanol as solvent in a pressurized glass reactor and treated for 30 minutes with 0.45 L/h of hydrogen. At 50°C and a pressure of 4 bars, a gas mixture consisting of 1.3 L/h of propylene, 2 L/h of hydrogen, 9.5 L/h of oxygen, and 0.5 L/h of nitrogen was then introduced.

From the analysis by gas chromatography, a volume fraction of 0.06% of propylene oxide was found after 12 hours in the off-gas stream of 13.4 L/h. After 22 hours, no more propylene oxide could be detected.

Actual Example 4

This example explains the process according to the invention for the one-stage production of propylene oxide from propylene, hydrogen, and oxygen on the catalyst produced according to Actual Examples 1 and 2 with methanol as the solvent. Here the "fat" method is used, i.e., with an excess of propylene.

2 g of catalyst from Actual Example 2 was suspended with continuous stirring in 1,650 mL of methanol as solvent in a glass pressurized reactor. At 60°C and a pressure of 5 bars, a gas mixture of 5 L/h of propylene, 0.25 L/h of hydrogen, 1 L/h of oxygen, and 0.5 L/h of nitrogen was then introduced.

In the off-gas stream of 6.8 L/h, analysis by gas chromatography showed the presence of 0.30 vol.% of propylene oxide after 44 hours, 0.68 vol.% of propylene oxide after 139 hours, 0.50 wt.% of propylene oxide after 270 hours, and 0.32 vol.% of propylene oxide after 360 hours. This also demonstrates that, by the use of the process according to the invention, propylene oxide can be produced by heterogeneous catalysis over a much longer period of time.

In separate experiments, it could be established that a gas mixture consisting of 5 L/h of propylene, 0.25 L/h of hydrogen, and 1 L/h of oxygen does not constitute an explosive mixture.

CLAIM(S)

1. Process for the production of epoxides from olefins, hydrogen, and oxygen with the use of an oxidation catalyst based on titanium or vanadium silicalites with a zeolite structure and a content of 0.1-20 wt.% of one or more platinum metals selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, and platinum, in which the platinum metals are present in each case in at least two different bond energy states, and possibly in the presence of an inert carrier gas selected from the group consisting of nitrogen, noble gases, carbon dioxide, and C_1 - C_8 -hydrocarbons, where the molar ratio of hydrogen to oxygen is 1:1-1:10 and the molar ratio of inert carrier gas to olefin can be as much as 20:1, characterized in that the molar ratio of oxygen to olefin or to the sum of olefin and any C_1 - C_8 -hydrocarbon which may be present as an inert carrier gas is less than 1:3-1:20.

2. Process for the production of epoxides according to Claim 1 in the presence of an inert carrier gas selected from the group consisting of nitrogen and saturated C_1 - C_8 -hydrocarbons, where the molar ratio of inert carrier gas to olefin is 1:50-20:1.

3. Process for the production of epoxides according to Claim 2, characterized in that the molar ratio of oxygen to olefin or to the sum of olefin and any saturated C_1 - C_8 -hydrocarbons which may be present as inert carrier gas is 1:4-1:10.

4. Process for the production of epoxides according to Claims 1-3, where the epoxidation is carried out in the presence of water.

5. Process for the production of propylene oxide according to Claims 1-4.